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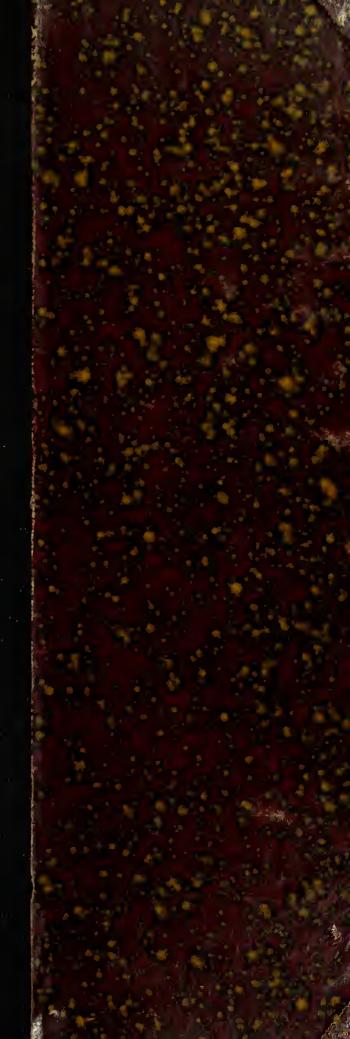
The Action of Metals on Complex

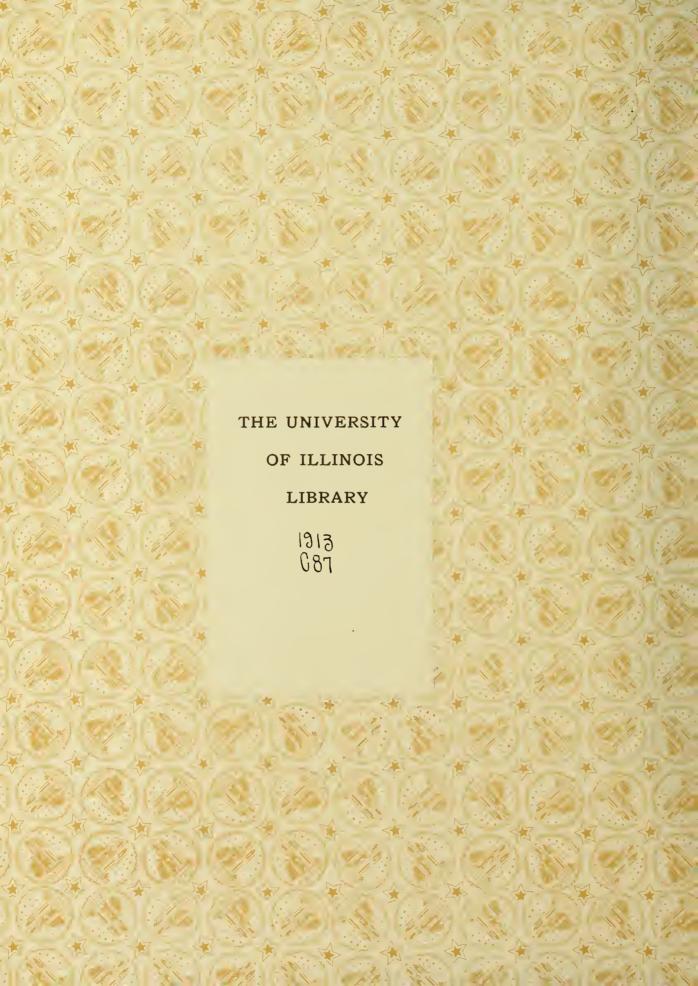
Cyanides in Aqueous Solutions

Chemistry

B. S.

1913









# THE ACTION OF METALS ON COMPLEX CYANIDES IN AQUEOUS SOLUTIONS

BY

Year - 3

MICHELE CROCE

**THESIS** 

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

**CHEMISTRY** 

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1913

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#### UNIVERSITY OF ILLINOIS

May 26th, 1913.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Michele Croce

ENTITLED The Action of Metals on Complex Cyanides in Aqueous Solutions.

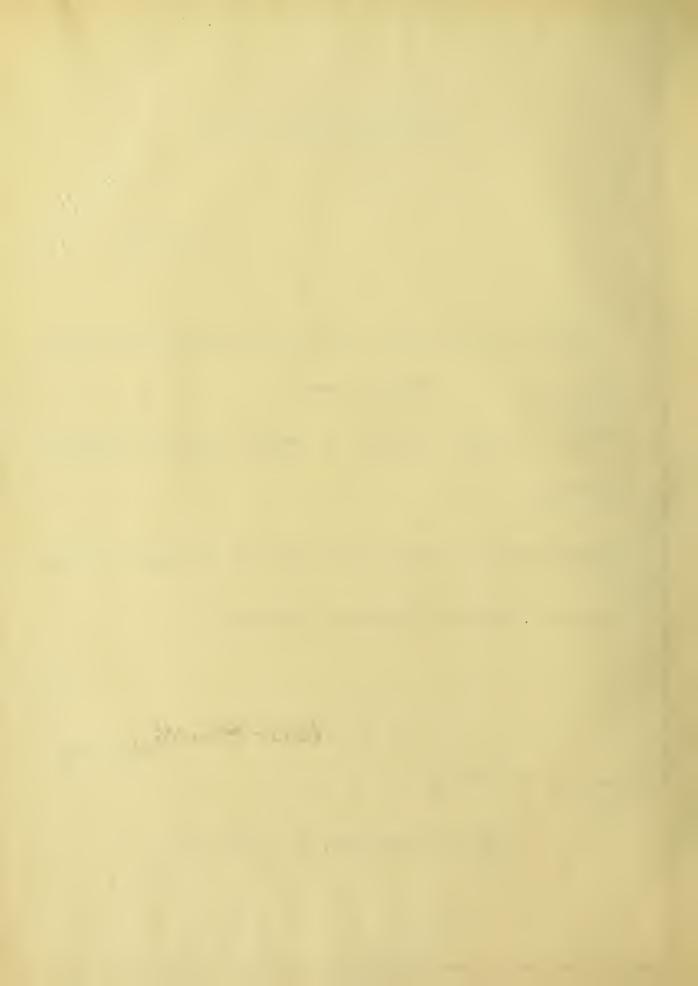
IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

GMCPSmith\_ Instructor in Charge

APPROVED: W. A. Noges

HEAD OF DEPARTMENT OF Chemistry



1913

THE ACTION OF METALS ON COMPLEX CYANIDES
IN AQUEOUS SOLUTIONS.

#### INTRODUCTION

It is a well known fact that in complex cyanides of the type Kx(Me Cyn) the metal atom Me does not generally lend itself to its ordinary chemical reactions. For example, potassium hydroxide and potassium chloride fail to precipitate silver oxide and silver chloride respectively from a solution of potassium silvercyanide, and potassium hydroxide does not precipitate mercuric oxide from a solution of potassium mercuriccyanide. However the complexes are to a certain extent dissociated in this manner:

$$HgCy_4^- \hookrightarrow Hg^{++} + 4Cy^-,$$
 $AgCy_2^- \hookrightarrow Ag^+ + 2Cy^-,$ 

as can be shown by the fact that hydrogen sulphide produces in such solutions a black precipitate of mercuric sulphide or silver sulphide.

Furthermore, G. McP. Smith in a paper on replacements of metals in aqueous solution ( Journal of American Chemical Society Vol. 27, 1905, page 540 ) states that cadmium is displaced from a solution of potassium cadmiumcyanide by a clean sheet of copper placed in the solution, especially upon warming. In a similar manner he showed that when silver is heated for a short time in a solution of potassium mercuric cyanide the following



- -

- -

reaction takes place

2Ag + Kangcy. ZKAgcya + Hg.

All the above facts show that in aqueous solution these complex cyanides are to a certain extent dissociated.

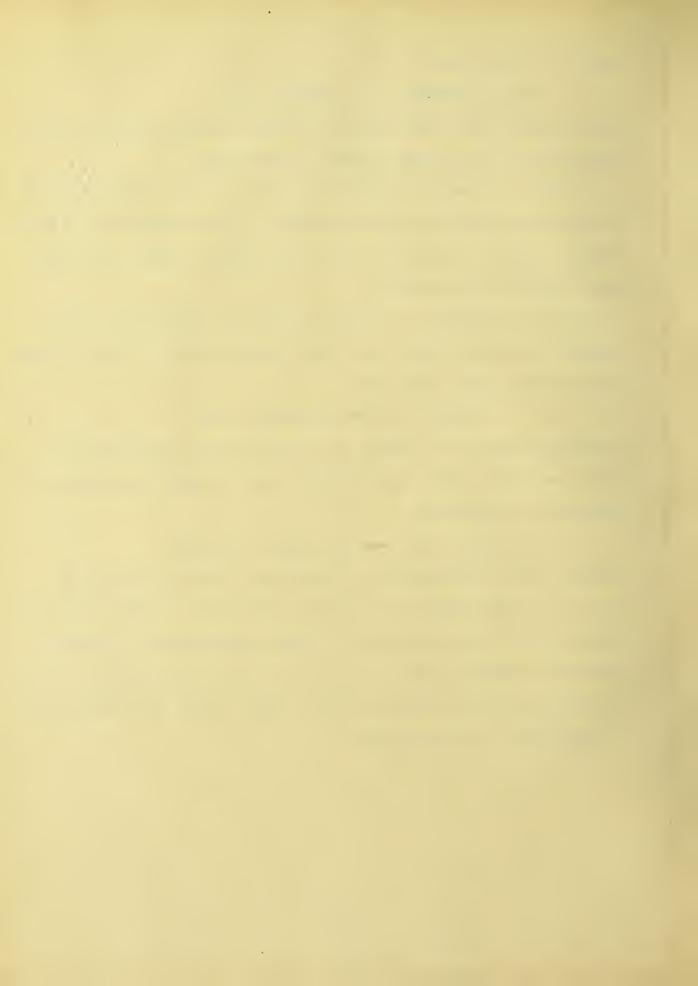
Since the complex cyanides mentioned above lend themselves to reversible metallic displacements, it was thought that other complex cyanides considered even more stable, might give analogous reactions with metals.

With this purpose in view a solution of potassium ferricyanide was heated with pure cobalt powder to see if the following reaction might take place:

A reaction was noticed which gave rise to the formation of a dark blue almost black precipitate, but the oxidizing action of potassium ferricyanide

4KsFeCy<sub>6</sub> + 2Co -- Co2FeCy<sub>6</sub> + 3K4FeCy<sub>6</sub>

(Lynch, Thesis for Bachelor of Arts, University of Illinois, 1908 L99), complicated this reaction to such an extent that this compound was found unsuitable for the investigation. However, potassium cobalticyanide is known to be much more stable than the corresponding ferricyanide, and for that reason the problem was attacked from the other side.



### EXPERIMENTAL PART

A

1. The Action of Metallic Cobalt upon Potassium Ferricyanide.

Ten grams of potassium ferricyanide were dissolved in 100 c.c. of water, and 2 grams of cobalt powder were digested in this solution on a steam bath for three hours. A reaction was noticed which gave rise to the formation of a bluish black precipitate. After a short time this precipitate became so abundant that it was inconvenient to work with the reaction. For the present this reaction was abandoned.

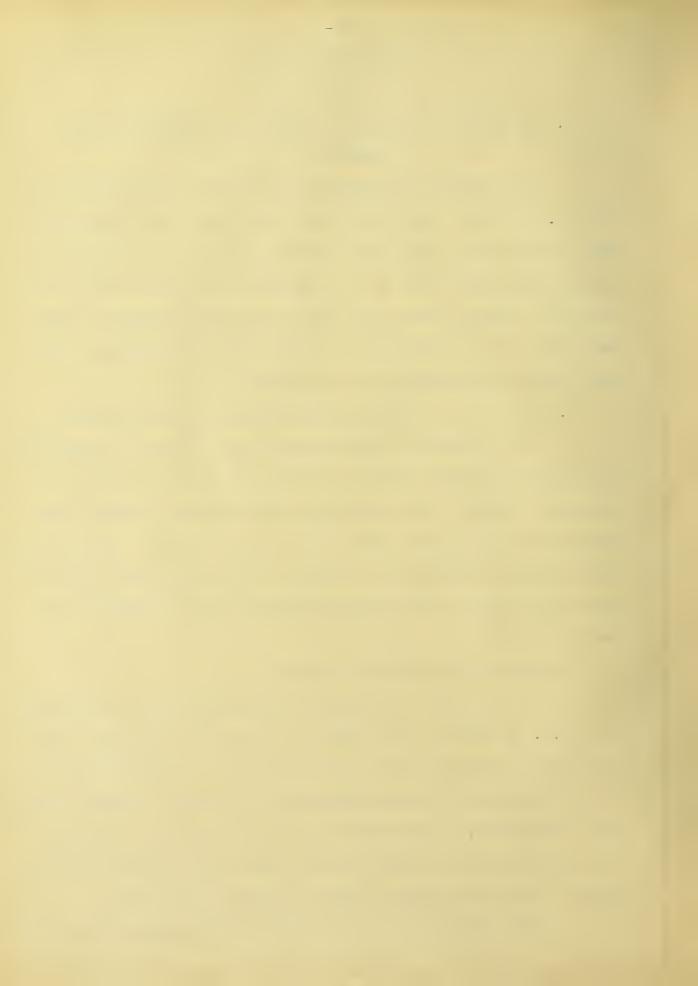
2. The Action of Metals upon Potassium Cobalticyanide.

a solution of cobalt nitrate with the calculated quantity of potassium cyanide. The resulting cobaltocyanide solution was oxidized by passing air thru it for thirty minutes. The salt was then crystallized from the solution, after acidifying the latter with acetic acid. Two recrystallizations were sufficient for its purification.

(a) The Action of Metallic Silver.

Five grams of potassium cobalticyanide were dissolved in 25 c.c. of water, a few grams of finely divided silver were added and the flask heated to a temperature of about 100° for twenty hours with a reflux condenser. No visible change occurred during this time. The contents were filtered thru a hardened filter paper and the residue washed free from potassium cobalticyanide. The washing were added to filtrate and saved.

The residue was treated with dilute hydrochloric acid

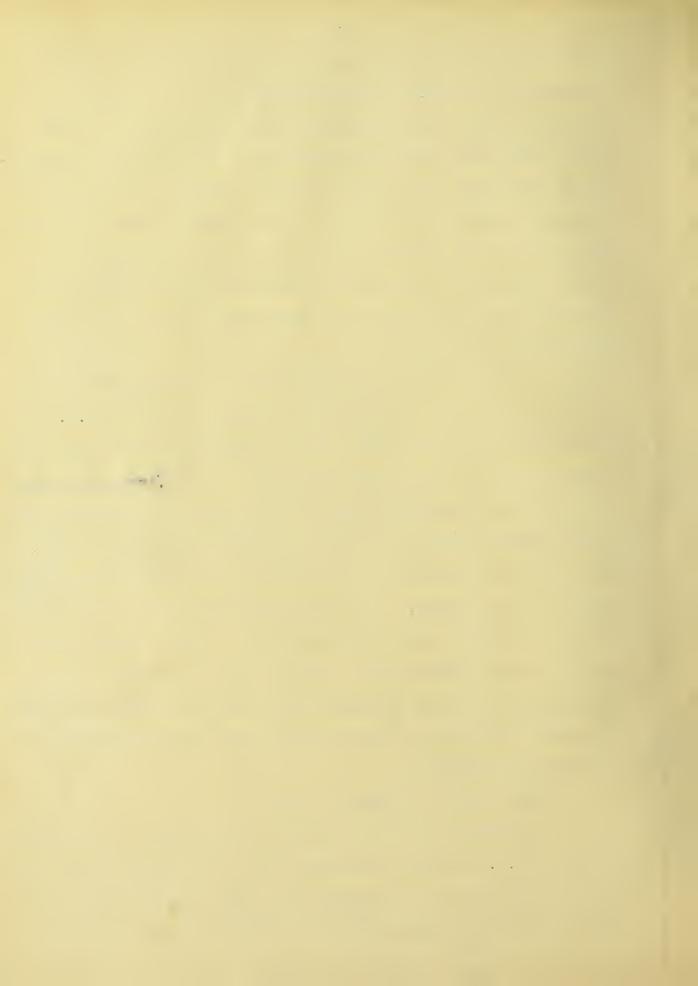


in the cold, filtered and washed, made alkaline with ammonium hydroxide and hydrogen sulphide passed thru it. A black precipitate formed, which imparted a blue coloration to a borax bead. This precipitate was dissolved in aqua regia and evaporated on the steam bath. The residue was taken up with as little water as possible and to this solution a small amount of potassium nitrite solution was added, then it was acidified with acetic acid and a crystalline yellow precipitate formed which signified that some cobalt must have come out from the potassium cobalticyanide solution.

tion after digestion with silver, was treated with 10 c.c. of concentrated sulphuric acid. A white precipitate came down. The mixture was heated in a casserole under a hood first gently and then somewhat vigorously to expel the excess of sulphuric acid. A pink residue remained. This residue was taken up in water. It did not go completely into solution, but a fine black powder settled at the bottom. The solution was filtered and the black residue saved for future investigation. To the filtrate the test for silver was applied. Only a trace was found. Other experiments similarly performed were carried out with all possible care, but failed to give any more than a mere indication of silver in the filtrate.

# (b) The Action of Metallic Iron.

Ten grams of the potassium cobalticyanide were dissolved in 50 c.c. of water and heated with a few grams of iron powder for ten hours on the steam bath. Some gas was evolved during this heating. The mixture was filtered thru a hardened



filter and the filtrate decomposed with sulphuric acid. This solution gave only a doubtful test for iron.

The residue was washed thoroughly and dissolved in dilute hydrochloric acid. This solution contained no cobalt.

(c) The Action of Metallic Cadmium.

Five grams of potassium cobalticyanide were dissolved in 25 c.c. of water and to this was added a few grams of cadmium shavings. The solution was heated over the steam bath for twenty-four hours, during this heating the liquid became somewhat lighter in color.

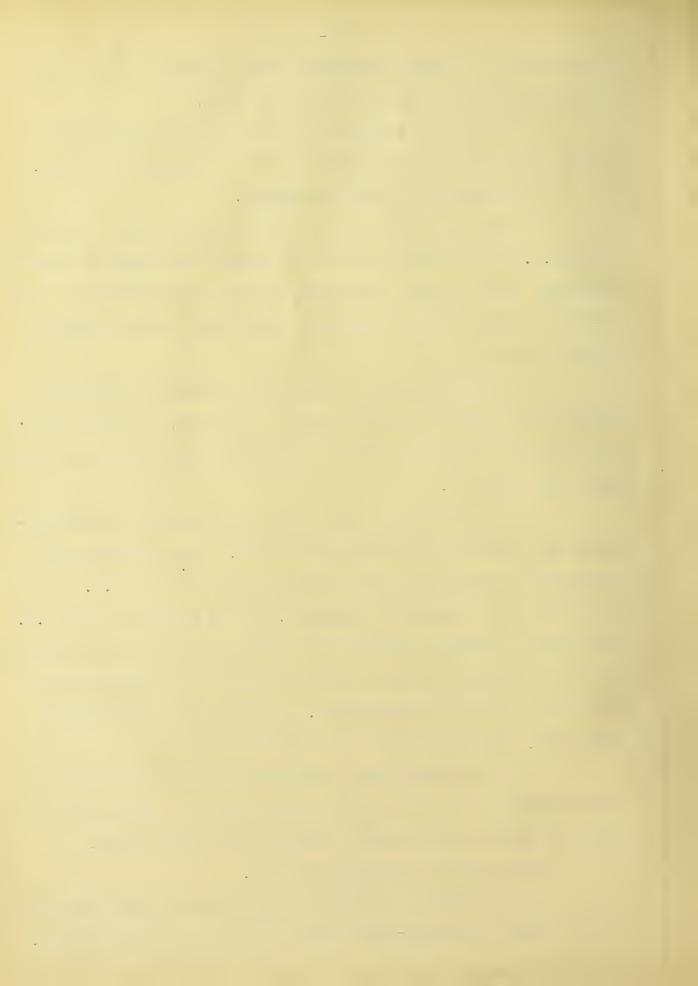
The mixture was filtered thru a hardened filter and hydrogen sulphide was passed thru the filtrate. A small amount of a yellow precipitate formed, indicating that some cadmium had gone into solution.

The residue was washed free from potassium cobalticyanide and dissolved in hydrochloric acid. This solution was
evaporated to dryness and the residue taken up in 4 c.c. of hydrochloric acid (specific gravity 1.12) and diluted to 100 c.c.
with water. Hydrogen sulphide was then passed in to precipitate.
The yellow precipitate was filtered off and the filtrate made
alkaline with ammonium hydroxide. A small black precipitate
came down, which was found to be cobalt sulphide.

This experiment was performed several times with slight modifications, but in all cases only a trace of cobalt and cadmium was found in the residue and filtrate respectively.

(d) The Action of Metallic Mercury.

A solution of potassium cobalticyanide was heated over a steam bath for twenty-four hours with some metallic mercury.



The mixture was filtered and the filtrate was treated with hydrogen sulphide. A small quantity of a black precipitate was formed.

The metallic mercury residue was washed with water placed in a little dish and then covered with dilute hydrochloric acid. A platinum wire was stuck in the mercury. If some cobalt had come out of the solution it would have amalgamated with mercury and then a gas would be evolved at the platinum wire. No gas was evolved, and it was therefore concluded that no cobalt was deposited from the solution.

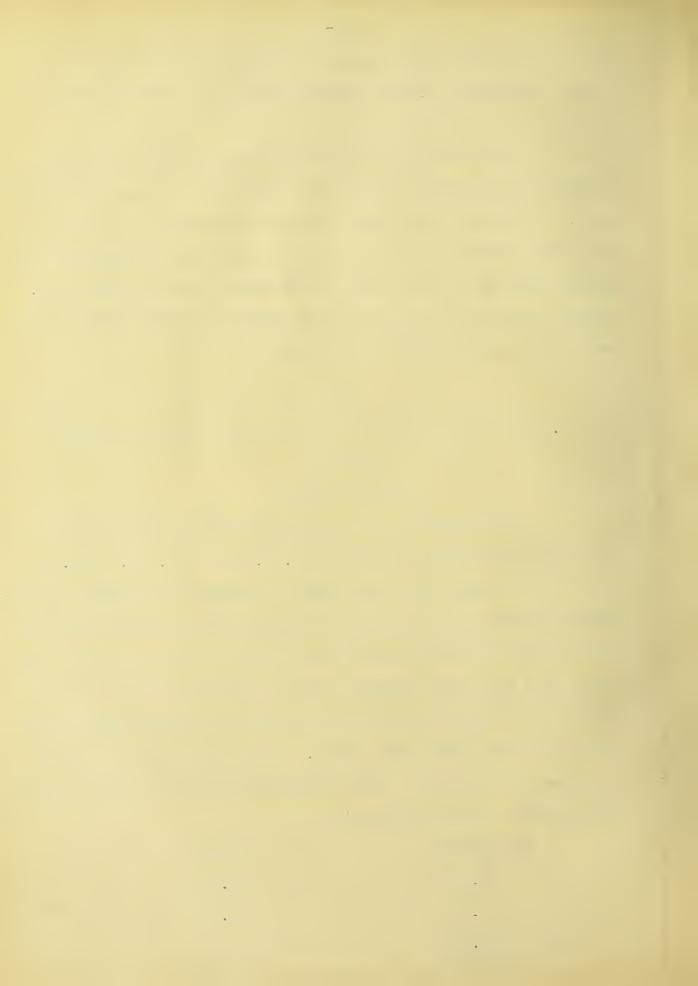
В

1. The Action of Metallic Silver upon Potassium Ferricyanide.

Previous Work.

In a paper on the action of metallic silver upon potassium ferricyanide solution, J. M. Eder, (J. pr. chem. 16 211 (1877)) states that he treated an excess of a fairly concentrated solution of potassium ferricyanide for several hours in the cold with freshly precipitated, finely divided silver. He found that the silver changed into a brownish-white substance and that the filtered solution contained potassium ferrocyanide, but that it was free from silver. The brownish white residue contained no potassium. Upon analyzing the solid residue Eder obtained the following results:

Calculated		Found
4 Ag	67.09 %	69.37 %
Fe	8.69	7.96
6 Cy	24.22 100.00 %	-



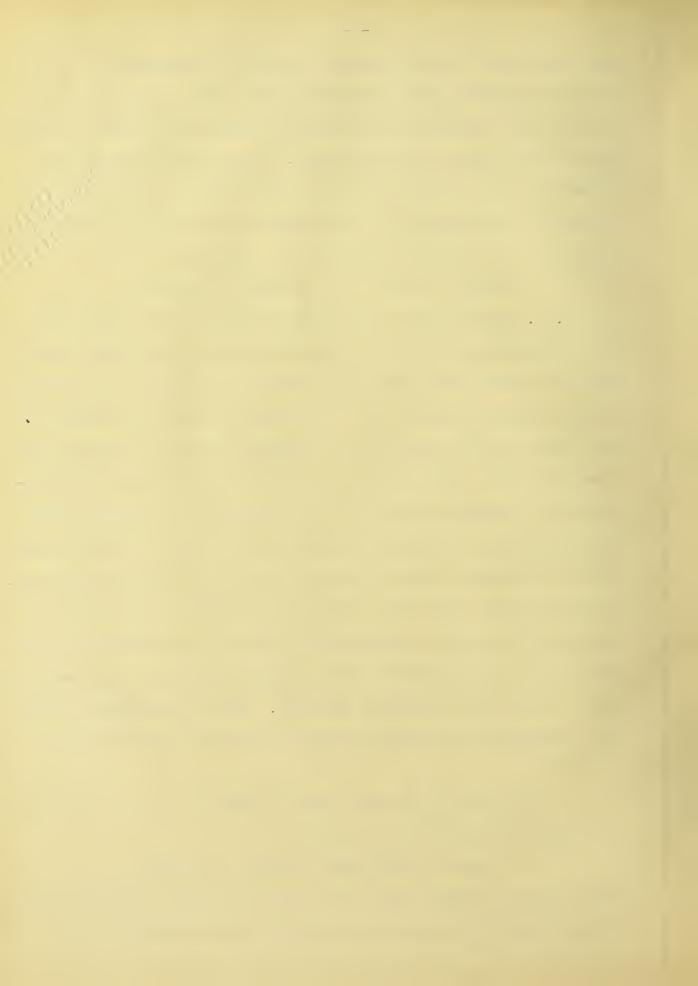
Eder concludes that the residue is silver ferrocyanide. He accounts for his high percentage of silver by assuming that some of the silver escaped from the action thru the protective influence of the deposit on its surface. Eder also determined the molecular ratio between potassium ferrocyanide in solution and the silver ferrocyanide in the residue, and found it to be exactly 3:1. He therefore deduced this equation-

4K3FeCy6 + 4Ag = 3K4FeCy6 + Ag4FeCy6

R. A. Lynch (Thesis for degree of Bachelor of Arts, L99
1908, University of Illinois) repeated Eder's experiment and obtained the same result when the reaction was allowed to proceed at the ordinary temperature. But when he caused the action to take place at the temperature of boiling water he obtained different results. Upon treating a solution of potassium ferricyanide with metallic silver at the temperature of boiling water Lynch obtained a solution from which silver could be precipitated by hydrochloric acid but not by means of potassium chloride. He subsequently found that silver ferrocyanide reacts with a hot solution of potassium ferrocyanide giving a solution from which silver may be precipitated with hydrogen sulphide or hydrochloric acid but not with potassium chloride. Upon evaporation a white salt crystallized out whose nature and composition he did not determine.

In view of the work done by Eder and Lynch it is evident that in the cold the reaction

4Ag + 4K3FeCy = Ag \* FeCy + 3K \* FeCy takes place, but that when the mixture is heated to about 100° c the products of the primary reaction react with each other to



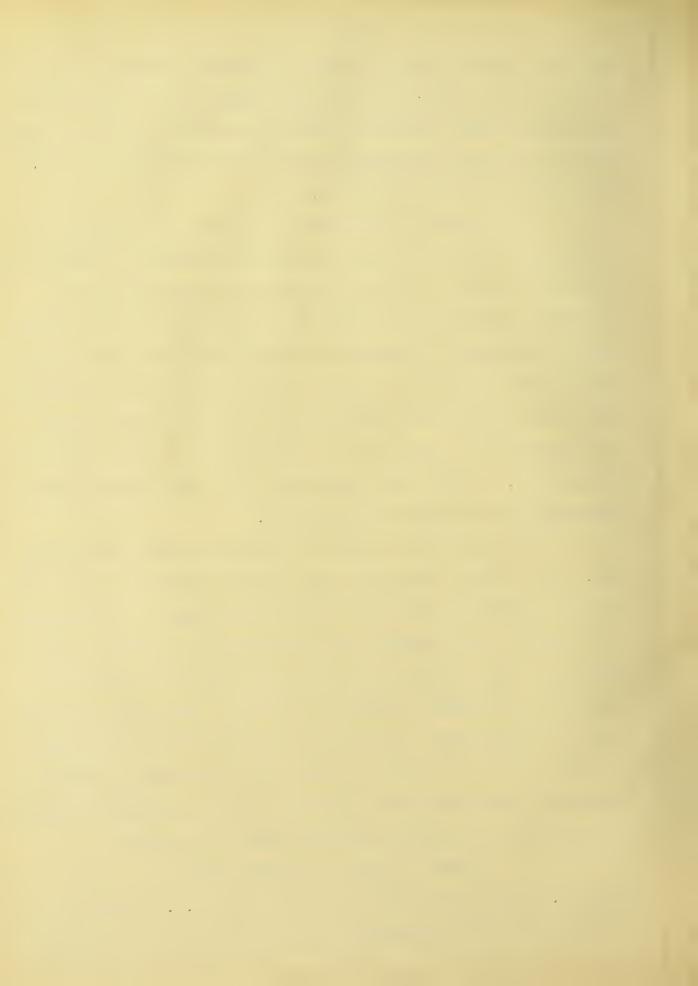
form some complex salt of silver. Since the purpose of this experiment is to study the nature and composition of the product of this secondary reaction it was only necessary to treat a solution of potassium ferrocyanide with silverferrocyanide, separate the complex salt and analyze it.

A solution of potassium ferrocyanide was treated for forty-eight hours on the steam bath with 15 grams of freshly precipitated silver ferrocyanide, obtained by the addition of potassium ferrocyanide solution to a solution of silver nitrate. After a few hours a greenish precipitate settled and the supernatant liquid was yellow in color. This solution was filtered and upon concentration small amounts of a red precipitate formed (iron hydroxide). The solution was filtered hot and allowed to crystallize. A white salt separated, while the mother liquor contained much potassium ferrocyanide.

The salt was filtered on a Buckner funnel and sucked dry. Then it was dissolved in the smallest amount of water and to this solution, strong ethyl alcohol was added. The potassium ferrocyanide still present was in this way precipitated, and filtered off. The filtrate was evaporated almost to dryness to drive off the alcohol, taken up in a very little water, and allowed to crystallize. The salt was recrystallized three times and then dried in an oven at 110°C. for eight hours. With the supposition that the salt is potassium silver cyanide the following procedure was adopted depending upon the equation

KAgCy2 + AgNo3 -> 2AgCN + KNo3.

About 0.3 gram of the salt was placed in 50 c.c. of water and warmed to about 80°, whereby all of the salt did not dissolve;



but upon adding a little ammonia the slight quantity of undissolved substance quickly went into solution. To this solution an excess of silver nitrate was added, after which the mixture was acidified with nitric acid. The flocculent white precipitate of silver cyanide was filtered off and weighed in a gooch crucible.

Potassium was determined in the filtrate as follows:
The excess of silver nitrate was precipitated with hydrochloric acid and filtered off. The filtrate was evaporated to dryness on the steam bath. The residue was evaporated with 15 c.c. of concentrated hydrochloric acid. This operation was repeated three times in order to completely remove the nitric acid. Then the white residue was taken up with water, filtered into a weighed platinum dish, the solution was evaporated to dryness on the steam bath, then dried more thoroughly on an electric hot plate, and finally heated gently until the ammomium salts were driven off. The potassium was finally weighed as the chloride.

Result of Analysis.

Percentage of Cyanogen

Calculated			Found
	I	a b	25.98 % 26.00
26.14 %	ΙΙ	(a b	26.71) 26.28
	III	a b	26.25 26.26
		Mean	26.15



## Percentage of Potassium

Calculated	Found		
70 50 %	a	19.18 %	
19.58 %	ъ	19.40	
	Mean	19.29 %	

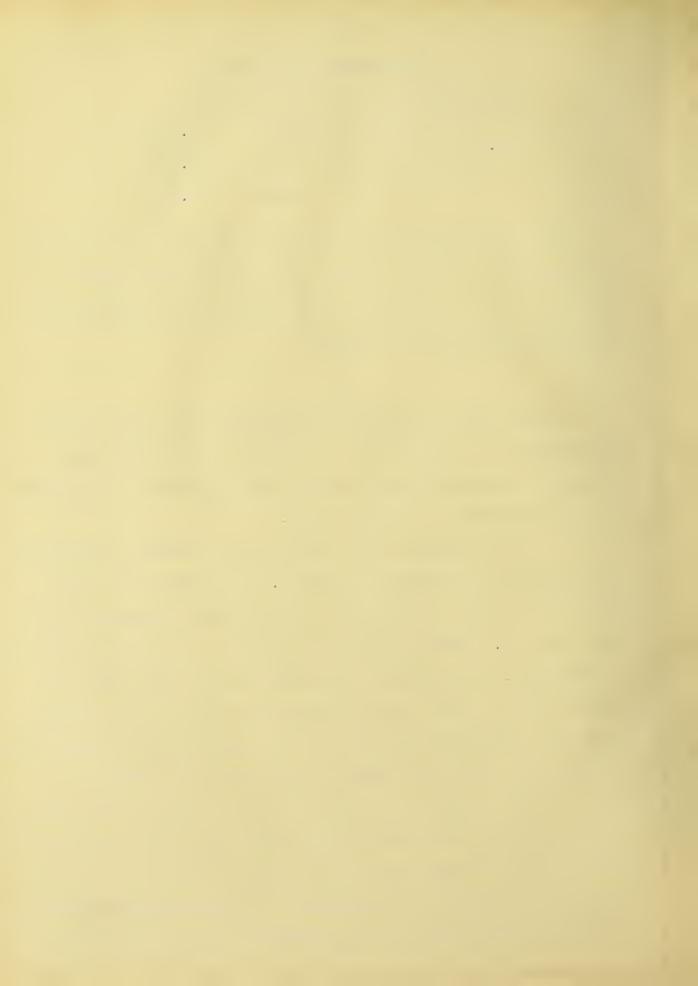
Since the results agree within the experimental error with the theoretical, it can be concluded that the salt formed by the action of silver ferrocyanide upon hot potassium ferrocyanide is potassium silver cyanide, KAgCy2.

C

The fact that potassium ferrocyanide reacts with silver ferrocyanide at a temperature of about 100°, suggested that potassium ferricyanide might also react with silver ferricyanide at the temperature of boiling water.

To investigate this reaction fifty grams of potassium ferricyanide were dissolved in 500 c.c. of water and to this solution was added the red silver ferricyanide prepared by precipitating 10.4 grams of silver nitrate with 6 grams of potassium ferricyanide. This mixture was heated on the steam bath for thirty hours. A fine green precipitate settled at the bottom, while the supernatant liquid was of a greenish yellow color. The solution was shaken from time to time during the heating.

The mixture was filtered, but the filtrate was not very clear even after five filtrations. The liquid was therefore made alkaline with potassium hydroxide, which gave rise to the precipitation of yellow iron hydroxide. The solution was filtered once more, after which it was concentrated on the steam bath.



More of the red iron hydroxide was formed, and upon evaporating almost to dryness the red precipitate was covered with a layer of white crystals. In lifting the solid layer from the bottom of the casserole a strong smell of ammonia was noticed.

The residue was dissolved in water, filtered, and allowed to crystallize. Crystals of potassium ferrocyanide came down. The mother liquor was concentrated three times and allowed to crystallize and in all cases the yellow potassium ferrocyanide crystallized out. Finally ethyl alcohol was added to the mother liquor and a white precipitate formed. This white precipitate did not contain any silver; it was filtered off and the filtrate was concentrated and allowed to crystallize. About five grams of a white substance were obtained. The amount being very small no recrystallization was attempted. This salt was dried between filter paper and finally in an oven at 110° for four hours. Then it was analyzed in the same manner as the salt obtained from the corresponding ferrocyanides.

In this case it was also necessary to add a little ammonia in order to dissolve the salt, and even after the addition of ammonia the solution was somewhat turbid. This, however, was accounted for by the fact that the salt was not pure.

Results of the Analysis

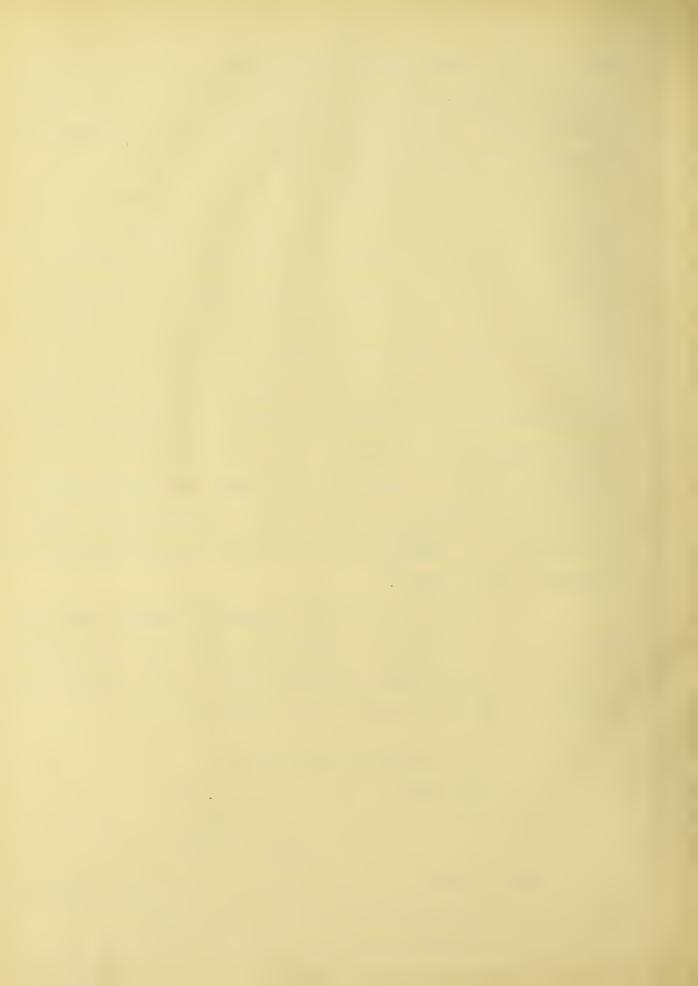
CN found I a 23.59 %

b 23.88

Mean 23.74 %

The low values obtained in this case are probably due to the fact that the salt was not purified before the analysis.

It is seen from the above experiments that potassium



ferricyanide in aqueous solution is reduced upon being heated with silver ferricyanide, with the formation of potassium ferrocyanide and a complex silver salt, which is probably potassium silver cyanide. The reaction is very complicated, and will be further investigated.





